



TITLE:

Synthesis and properties of compounds having novel structure containing heavier group 14 elements/ Synthesis of the first stable phosphorusbismuth double-bond compound/ Synthesis and properties of the first platinum-dichalcogenide complexes (BIOORGANIC CHEMISTRY - Organoelement Chemistry)

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Scope of Research

Organic chemistry has been developed as that of second-row elements such as carbon, oxygen, and nitrogen so far, while the synthesis and isolation of the heavier congeners of typical organic molecules as stable compounds have been one of "dreams" for organic chemists. Our main research interest is the elucidation of the resemblance and difference in structures and reactivities between organic compounds and the corresponding heavier congeners. These studies are interesting from the standpoints of not only fundamental chemistry but also opening the way to more extensive application of main group chemistry. Organic synthesis mediated by biocatalysts are also studied.

Research Activities (Year 2001)

Presentations

Synthesis and properties of compounds having novel structures containing heavier group 14 elements, Tokitoh N, Sasaki T, Sasamori T, Takeda N, 6th Int. Conference on Heteroatom Chem., 25 Jun. Nakata N, Takeda N, Tokitoh N, Xth Int. Conference on the Coord. and Organomet. Chem. of Germanium, Tin and Lead, 10 Jul. Other 21 papers were presented.

Synthesis and reactivity of low-coordinated compounds containing group 15 elements, Sasamori T, Takeda N, Tokitoh N, XVth Int. Conference on Phosphorus Chem., 31 Jul. Other 4 papers were presented.

Synthesis and reactivity of platinum-dichalcogenido complexes, Nagata K, Takeda N, Tokitoh N, XVth Int. Conference on Phosphorus Chem., 2 Aug. Other 3 papers were presented.

Organic synthesis mediated by biocatalysts, Kawai Y, Hayashi M, Tokitoh N, Molecular Chirality 2001, 8 Jun. Yamanaka R, Nakamura K, Hori M, *et al*, Biotrans'01, 4 Sep. Other 14 papers were presented.

Others, 16 papers were presented.

Grants

Tokitoh N, Systematic studies on the synthesis, structures, and properties of aromatic compounds containing heavier group 14 elements, Grant-in-Aid for Scientific Research (A) (2), 1 Apr 1999 - 31 Mar 2002.

Tokitoh N, Development of synthetic methods for novel species on the basis of the concept of steric protection, Grant-in-Aid for Scientific Research on Priority Areas (A) (2), 1 Apr 1999 - 31 Mar 2002.

Kawai Y, Studies on the novel enzymatic reaction mechanisms taking into account the enzyme fluctuations, Grant-in-Aid for Scientific Research (C) (2), 1 Apr 2000 - 31 Mar 2002.

Takeda N, Synthesis of novel multiple-bond species of silicon by taking advantage of silylene-isocyanide complexes and their properties, Grant-in-Aid for Encouragement of Young Scientists, 1 Apr 2001 - 31 Mar 2003.

Topics

Synthesis and properties of compounds having novel structure containing heavier group 14 elements

In recent decades, the chemistry of compounds having novel structure containing heavier group 14 elements has been extensively studied. We have developed novel steric protection groups, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt), which are very useful for the kinetic stabilization of various highly reactive species of main group elements.

We succeeded in the synthesis of the first stable 2-germanaphthalene, 9-silaanthracene, germacyclopropabenzene, and silylborane-isocyanide complexes by taking advantage of Tbt group, and elucidated their interesting properties. Especially, it is noteworthy that the 2-germanaphthalene is the first neutral germaaromatic compound.

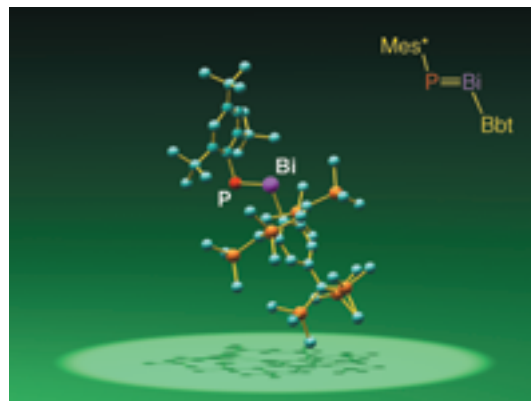


Synthesis of the first stable phosphorus-bismuth double-bond compound

In recent years there has been much interest in compounds with a double bond between heavier group 15 elements. However, there is no heteronuclear doubly bonded system between phosphorus and bismuth, *i. e.*, phosphabismuthene. We now report the synthesis of the first stable phosphabismuthene by taking advantage of the Bbt group, which is also effective for the synthesis of distibene, dibismuthene, and stibabismuthene.

Condensation of Mes*PH₂ with BbtBiBr₂ using 1,8-diazabicyclo[5.4.0]undec-7-ene as a base afforded the

first stable phosphabismuthene Mes*P=BiBbt, which is also the first stable double-bond compound between the third and sixth row main group elements.

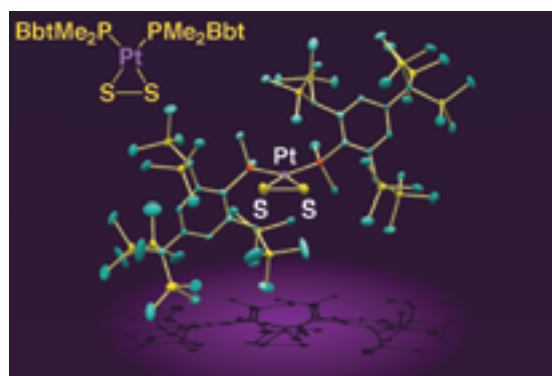


Molecular structure of Mes*P=BiBbt.

Synthesis and properties of the first platinum-dichalcogenido complexes

Much attention has been paid to transition metal complexes with a disulfur or diselenium ligand, which are heavier congeners of well-studied dioxygen complexes. However, the platinum complexes with disulfur and diselenium (*i. e.*, PtE₂ ring systems) remain unknown.

The first platinum disulfur and diselenium complexes have been synthesized by taking advantage of new bulky phosphine ligands ArMe₂P (Ar = Tbt or Bbt). These complexes have a square planar geometry and a three-membered PtE₂ (E = S, Se) ring.



Molecular structure of (BbtMe₂P)₂PtS₂.

Awards

Nakata N, Symposium Poster Award, 6th Symposium of the Soc. of Silicon Chem., Jpn., Reactivity of kinetically stabilized 2-germanaphthalene, the Soc. of Silicon Chem., Jpn., 16 Nov.

Nagata K, Symposium Lecture Award, 80th Annual Meeting of the Chem. Soc. Jpn., Syntheses and properties of novel three-membered cyclic platinum complexes having a dichalcogenido ligand, the Chem. Soc. Jpn., Dec.

Kawai Y, 5th Japanese Symposium on the Chem. of Biocat., Best Poster Award, Characterization of nitroalk-

ene reductases, The Committee of 5th Japanese Symposium on the Chem. of Biocat., 14 Dec.

Yamanaka R, 5th Japanese Symposium on the Chem. of Biocat., Best Poster Award, Asymmetric reduction of ketones by cyanobacteria, The Committee of 5th Japanese Symposium on the Chem. of Biocat., 13 Dec.

Yamaguchi H, 5th Japanese Symposium on the Chem. of Biocat., Best Poster Award, Purification and characterization of α -keto ester reductase from streptomyces coelicolor A3(2), The Committee of 5th Japanese Symposium on the Chem. of Biocat., 14 Dec.